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ABSTRACT

Aeronautic and space applications require the development of chemical sensors with capabilities beyond those of commercially available sensors. Areas of interest include launch vehicle safety monitoring, emission monitoring, and fire detection. This paper discusses the needs of aeronautic and space applications and the point-contact sensor technology being developed to address these needs. The development of these sensors is based on progress in two types of technology: 1) Micromachining and microfabrication technology to fabricate miniaturized sensors. 2) The development of high temperature semiconductors, especially silicon carbide. Sensor development for each application involves its own challenges in the fields of materials science and fabrication technology. The number of dual-use commercial applications of this microfabricated gas sensor technology make this area of sensor development a field of significant interest.

INTRODUCTION

Aeronautic and space applications require the development of chemical sensors which operate in a number of environments. Three areas of particular interest are safety monitoring, emission monitoring, and fire detection. Each of these areas are the subject of effort throughout NASA to, for example, improve safety and decrease the cost of space travel, significantly decrease the amount of emissions produced by aeronautic engines, and improve the safety of commercial airline travel. Each area of application has vastly different problems associated with the measurement of chemical species. However, the development of a common base technology can address the measurement needs of a number of applications.

In launch vehicle safety applications, detection of low concentrations of hydrogen at potentially low temperatures is important for applications involved with, for example, operation of the Space Shuttle. In 1990, the leaks on the Space Shuttle while on the launch pad temporarily grounded the fleet until the leak source could be identified. The method of leak detection used was a mass spectrometer connected to an array of sampling tubes placed throughout the region of interest. Although able to detect hydrogen in a variety of ambient environments, the mass spectrometer had a delay time associated with its detection of a leak and pinpointing the exact location of the leak was problematic.

In response to the hydrogen leak problems, NASA endeavored to improve propellant leak detection capabilities during assembly, pre-launch operations, and flight. The objective has been to reduce the operational cost of assembling and maintaining hydrogen delivery systems with automated detection systems. In particular, efforts were made to develop an automated hydrogen leak detection system using point-contact hydrogen sensors. However, no commercial sensors existed that operated satisfactorily in this and other space related applications. The reason for this is the conditions in which the sensor must operate.

The hydrogen sensor must be able to detect hydrogen from low concentrations through the lower explosive limit (LEL) which is 4% in air. The sensor must be able to survive exposure to 100% hydrogen without damage or change in calibration. Further, the sensor may be exposed to gases emerging from cryogenic sources. Thus, sensor temperature control is necessary. Operation in inert environments is necessary since the sensor may have to operate in areas purged with helium. Ability to operate in a vacuum is desirable. Being able to multiplex the signal from a number of sensors so as to "visualize" the magnitude and location of the hydrogen leak is also desired. If a number of sensors are to be placed in an area, then size, weight, and power consumption for each sensor becomes an issue. Commercially available sensors, which often needed oxygen to operate or depended upon moisture (1), did not meet the needs of this application and thus the development of new types of sensors was necessary (2).

The development of a new class of sensors is also necessary for the monitoring of emissions from aircraft engines. The control of emissions from aircraft engines is an important component of the development of the next generation of these engines. The ability to monitor the type and quantity of emissions being generated by an engine is important in not only controlling those emissions but also in determining the status of the engine. Ideally, an array of sensors placed in the emissions stream close to the engine could provide information on the gases being emitted by the engine. However, there are very few sensors available commercially which are able to measure the components of the emissions of an engine in-situ. The harsh conditions and high temperatures inherent near the reaction chamber of the engine render most sensors inoperable.

A notable exception to this limitation in sensor technology is the commercially available oxygen sensor presently in use in automobile engines (3). This sensor, which is based on the changes in the properties of zirconium dioxide (ZrO_2) upon reaction with oxygen, has been instrumental in decreasing automotive engine emissions. However, comparable sensors for other components of the gas stream do not exist: sensitive monitoring of emissions of nitrogen oxides, hydrogen, and hydrocarbons is not presently possible in-situ with point-contact sensors placed near the engine. Even the traditional ZrO_2 based sensor has sensitivity limits as well as size, weight, and power consumption requirements which prevent its use in some applications.

In emission monitoring applications, the sensor must operate at high temperatures with exposure to low concentrations of the gases to be measured. Although the measurement of nitrogen oxides is important in these applications, the measurement of other gases present in the emission stream such as hydrogen, hydrocarbons and oxygen is also of interest. The measurement range depends on the gas and the engine but generally the detection of nitrogen oxides, hydrogen, and hydrocarbons may be necessary at sensitivities of less than 200 ppm with corresponding measurements of oxygen from less than 1% to near 20%. The sensors should be small so as not to interfere with the flow of gases in the engine or become significant projectiles if dislodged from their measuring site and emitted into the engine.

In fire safety applications, fire detection equipment presently used in the cargo holds of many commercial aircraft relies on the detection of smoke. Although highly developed, these sensors are subject to false alarms. These false alarms may be caused by a number of sources including: changes in humidity, condensation on the fire detector surface, contamination from animals, plants, or other contents of the cargo bay (4). A second method of fire detection to complement existing techniques, such as the measurement of chemical species indicative of a fire, will help reduce false alarms and improve aircraft safety. Although, many chemicals species are indicative of a fire, two species of interest are carbon monoxide and carbon dioxide (5).

In order to meet the needs of these applications, a new generation of sensor technology must be developed. This paper discusses point-contact sensor technology being developed to address these needs. The development of these sensors is based on progress in two types of technology: 1) Micromachining and microfabrication technology to fabricate miniaturized sensors, and 2) The development of high temperature semiconductors, especially silicon carbide, to provide electrical components and sensors operable at the temperatures of interest. Using these technologies, point-contact sensors are being developed to measure hydrogen (H_2), hydrocarbons (C_xH_y), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2) and oxygen (O_2). The detection of each type of gas involves its own challenges in the fields of materials science and fabrication technology.

This paper presents an overview of microfabricated chemical sensor technology and high temperature electronics. These technologies are used, where appropriate, to develop H_2, C_xH_y, NO_x, CO, CO_2 and O_2 sensors. A description is given of each sensor type and its present stage of development. The silicon (Si) based hydrogen sensor is at a relatively mature stage of development while the state of development of the other sensors ranges from the proof of concept level to prototype stage. The number of dual-use commercial applications make this general area of sensor development a field of significant interest.

MICROFABRICATION AND MICROMACHINING TECHNOLOGY

A significant number of silicon-based microfabrication processes have been derived from the advancements in the integrated circuit (IC) industry. Of the various processing techniques, lithographic reduction, thin film metallization, photoresist patterning, and chemical etching have found extensive chemical and biological applications, particularly in sensor-related development. These processes allow the fabrication of very small sensor structures. The ability to batch process these sensors using presently available semiconductor processing techniques significantly decreases the fabrication costs per sensor. However, these processes produce mainly two-dimensional planar structures, which have limited application. By combining these processes with micromachining technology, three-dimensional structures can be formed which have a wider range of application to chemical sensing technology. Micromachining technology is generally defined as the means to produce three-dimensional structures using both bulk and surface micromachining techniques. The techniques used in micromachining fabrication include chemical anisotropic and dry etching, the sacrificial layer method, and LIGA (lithographic, galvanoforming, absorbing).

Chemical anisotropic etching is an etching procedure that depends on the crystalline orientation of the substrate. For silicon etching, potassium hydroxide (KOH) and tetramethyl ammonium hydroxide (TMAH) solutions are most commonly used as etching agents. Dry etching processes include ion milling, plasma etching, reactive ion etching, and reactive ion beam etching. These dry etching processes are not dictated or limited by the crystalline structure. However, although not many chemicals are required, the capital equipment cost of any of these dry etching processes is relatively high.

The sacrificial layer method employs a deposited underlayer that can be chemically removed. The sacrificial layer method has been used to create cantilever type structures for physical sensor and actuator applications. This technique can be used to make a chamber electrode structure to protect the integrity of the sensor element. LIGA techniques have been used to produce high aspect ratio multistructures. These microstructures can be used to define volumes as well as for microanalytical elements such as microcapillary structures.

For many applications, temperature control is necessary. Incorporation of a heating element and a temperature detector allows feedback control of the operating temperature. In these microstructures, a small thermal mass is desirable in order to minimize heat loss and heat energy consumption. This is accomplished by selective removal of the silicon substrate producing a suspended diaphragm structure.

This sensor processing is done using Si either as a semiconductor that is part of an electrical circuit or as a substrate on which a structure is built. If Si is used as a substrate, the temperature range of the sensor can be rather broad: from cryogenic temperatures to above 600°C. However, if Si is to be used as part of the electrical circuit, the temperature range is limited to below 300°C. Thus, for this and other applications, high temperature electronics must be developed. The most advanced high temperature electronic material is silicon carbide (SiC). An overview of SiC-based high temperature electronics is given in the next section.

SiC-BASED HIGH TEMPERATURE ELECTRONICS

Silicon carbide based semiconductor electronic devices and circuits are presently being developed for use in high-temperature, high-power, and/or high-radiation conditions under which conventional semiconductors cannot adequately perform. Silicon carbide's ability to function under such extreme conditions is expected to enable significant improvements to a far ranging variety of applications and systems. These range from greatly improved high-voltage switching for energy savings in public electric power distribution and electric vehicles to more powerful microwave electronics for radar and communications to sensors and controls for cleaner-burning more fuel-efficient jet aircraft and automobile engines (6).

Silicon carbide occurs in many different crystal structures (called polytypes) with each crystal structure having its own unique electrical and optical properties. The electrical properties of the more common SiC polytypes are compared to the properties of silicon and GaAs in Table I, which was constructed from data in references 7-14. In many device applications, SiC's exceptionally high breakdown field (> 5 times that of Si), wide band gap energy (> 2 times that of Si), high carrier saturation velocity (> 2 times that of Si), and high thermal conductivity (> 3 times that of Si) could lead to substantial performance gains, in spite of the low carrier mobility disadvantages.

Complex electronics and sensors are increasingly relied upon to enhance the capabilities and efficiency of modern jet aircraft. Many of these electronics and sensors monitor and control vital engine components and aerosurfaces that operate at high temperatures. However, since today's silicon-based electronics technology cannot function at high temperatures, these electronics must reside in environmentally controlled areas. This necessitates the use of long wire runs between the sheltered electronics and the hot-area sensors and controls or the fuel-cooling of the electronics and sensors located in high-temperature areas. Both of these low-temperature-electronics approaches suffer from serious drawbacks, as the wire runs add a substantial amount of weight, fuel cooling has harmed aircraft fuel efficiency, and both have negatively impacted aircraft reliability.

A family of high temperature silicon carbide electronics and sensors that could function in hot areas of the aircraft would alleviate the above-mentioned technical obstacles to enable substantial aircraft performance gains. Uncooled operation of 300 - 600°C SiC electronics and sensors mounted in the aircraft hot areas would save weight and increase reliability by replacing hydraulic controls with "smart" electromechanical controls. SiC-based distributed control electronics would eliminate 90 % of the wiring and connectors needed in conventional sheltered-electronic aircraft control systems. This is extremely crucial given the fact that wiring and connector problems are the most frequent cause of propulsion maintenance activity and downtime in commercial aircraft today. The U. S. Air Force has estimated that advanced SiC control electronics implemented on an F-16 fighter would allow the aircraft to shed as much as 800 pounds of weight, operate with increased capabilities and fuel efficiency, and operate more reliably with less maintenance and downtime (15).

	Si	GaAs	6H-SiC	4H-SiC	3C-SiC
Bandgap (eV)	1.1	1.42	3.0	3.2	2.3
Breakdown Field @ 10^{17} cm^{-3} (MV/cm)	0.6	0.6	3.2	3	> 1.5
Electron Mobility @ 10^{16} cm^{-3} (cm^2/ V-s)	1100	6000	370	800	750
Saturated Electron Drift Velocity (cm/s)	10^7	10^7	2×10^7	2×10^7	2.5×10^7
Thermal Conductivity (W/cm-K)	1.5	0.5	4.9	4.9	5.0
Hole Mobility @ 10^{16} cm^{-3} (cm^2/ V-s)	420	320	90	115	40

Table I: Comparison of selected semiconductor room temperature physical properties.

SiC electronics and sensors offer similar improvements to commercial jetliners, where increased fuel efficiency, weight savings, and reduced pollution carry particularly large economic and environmental payoffs over an aircraft's multi-decade operational lifetime. It has been speculated that the economic savings value will be in the millions of dollars per aircraft.

Therefore, silicon carbide electronics and sensors that could function while mounted in hot engine and aerosurface areas of an aircraft would enable substantial weight savings, increased jet engine performance, and increased reliability. Use of SiC electronics and devices in other applications such as in the fields of power distribution, automobiles, and communications and radar could have correspondingly significant effects on the operation of these systems.

SENSOR DEVELOPMENT

The needs of aeronautic and space applications require the development of new sensor technology to operate in environments in which conventional sensors are inoperable or do not provide the required measurements. These applications require operation in a variety of conditions: from cryogenic temperature to above 600°C, from inert environments to corrosive engine conditions, and from the detection of one gas over a wide concentration range to the detection of several gases over more narrow concentration ranges. Combined with this is the desire to minimize size, weight, and power consumption as well as decrease the cost of the sensor. In order to meet these needs, a flexible approach is necessary. Microfabrication and micromachining technology as well as the use of SiC semiconductor technology can address many of the needs of aeronautics and space applications.

Microfabrication and micromachining allows the fabrication of a variety of structures. Size, weight, and power consumption are minimized by microfabricating the structure while micromachining allows complex shapes to be incorporated into a small region. A given structure can be tailor-made to measure different gases by changing, for example, the gas sensitive element. Batch processing using Si semiconductor technology can decrease cost per sensor and allow a large number of sensors to be produced in one series of processing. Silicon can be used as substrate or part of the electrical circuit. However, Si is not appropriate for sensor designs in which the substrate is an electrical component of the sensor and the sensor must operate at high temperature. Thus, the use of SiC is necessary in these applications.

The following reviews the application of microfabrication and micromachining technologies as well as SiC technology to develop sensors for the detection of a variety of gases. This work is done at NASA Glenn Research Center (GRC), Case Western Reserve University (CWRU), Makel Engineering Inc. (MEI), and Georgia Institute of Technology (GIT). The sensor design and sensing approach depends strongly on the application.

Si-Based Hydrogen Sensor Technology

One component of the sensor development program at NASA GRC and CWRU in conjunction with MEI involves the development of palladium (Pd) alloy Schottky diodes on silicon (Si) substrates. These sensors are designed to detect hydrogen in space applications. This type of sensor is based on metal-oxide-semiconductor (MOS) technology such as that used in the semiconductor electronics industry. The gas sensing MOS structures are composed of a hydrogen sensitive metal deposited on an oxide adherent to a semiconductor. This forms a Schottky diode in the case of a very thin layer of oxide. The most common MOS structure used for hydrogen detection is the Pd-SiO_2-Si structure. Hydrogen disassociates on the Pd surface and diffuses to the Pd-SiO_2 interface affecting the electronic properties of the MOS system (16). The use of pure Pd at near room temperatures as the hydrogen sensitive metal is problematic for several reasons. The most serious of these involves a phase change that occurs at high hydrogen concentrations which can lead to hysteresis or film damage.

Schottky diodes using Pd alloys as the hydrogen sensitive metal are presently being fabricated. The first generation of these sensors used palladium silver (PdAg). The use of PdAg in hydrogen sensing applications was pioneered by Hughes (17). Palladium silver has advantages over Pd. Palladium silver is more resistant to damage from exposure to high hydrogen concentration than Pd. Furthermore, the alloy has faster response times than Pd.

The sensor structure is shown in Figure 1. The structure includes a Pd alloy Schottky diode, a temperature detector, and a heater all incorporated in the same chip. The surface area of the Schottky diode is 6.1×10^{-3} cm^2 and the sensor dimensions are approximately 2.2 mm on a side. The response of the Schottky diodes was determined by measuring the diode's reverse current.

The properties of the PdAg sensor make it very useful for applications where sensing small amounts of hydrogen is necessary. The sensor responds in an inert environment (no oxygen) to the presence of hydrogen. The presence of oxygen decreases the sensor response but the sensor is still sensitive to low concentrations of hydrogen (18-19). The sensor

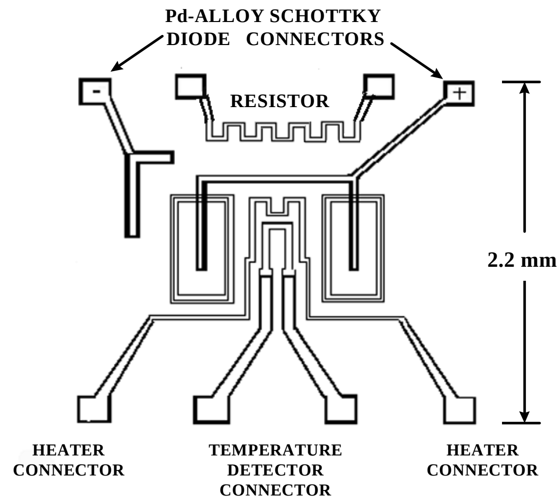


Figure 1. Schematic diagram of the Schottky Diode Hydrogen Sensor. The Pd alloy Schottky diode resides symmetrically on either side of a heater and temperature detector. The resistor has been added to the PdCr based sensor design.

response is large, rapid, and repeatable. If quick recovery is necessary, then the sensor should be operated in oxygen containing gases. If detection of the presence of hydrogen is required without rapid recovery, then this sensor can also be used in inert environments. The sensor responds to hydrogen across a wide concentration range with a signal and response time that is temperature dependent. This sensor can be used to monitor leaks in a multipoint leak detection scheme involving a number of these sensors. Further, this PdAg sensor has been shown to have a sensitivity and response comparable to that of a mass spectrometer (20).

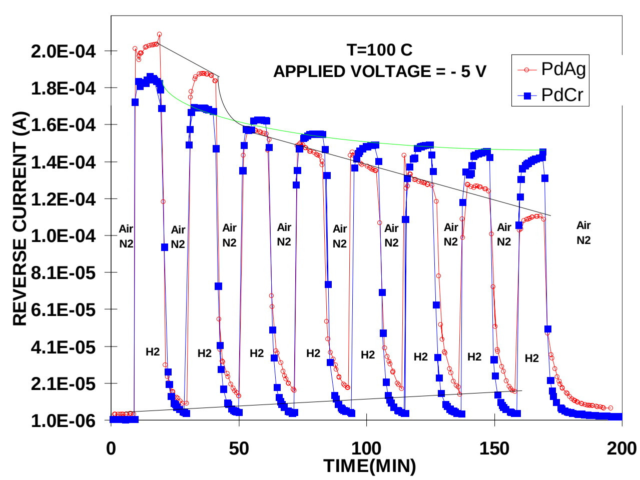


Figure 2. The response of PdAg and PdCr Schottky diode sensors at 100°C to repeated exposures of 9 minutes of air, 1 minute of nitrogen, 10 minutes of 100% hydrogen, and 1 minute of nitrogen. The PdCr diode shows a more repeatable baseline and a more stable response than the PdAg diode.

Although the PdAg sensor showed excellent properties for a number of applications, at higher temperatures and higher hydrogen concentrations its calibration changed and the sensor occasionally failed (18). Thus, the sensor behavior needed to be stabilized if it were to be exposed to 100% hydrogen as in the Shuttle application. This led to the development of the next generation of sensor. This sensor, which uses PdCr as the hydrogen sensitive alloy, is in its later stages of development. A comparison of the response to 100% hydrogen at 100°C of the two types of sensors is shown in Figure 2. The PdCr sensor is much more stable than the PdAg sensor in these conditions. The response of the PdAg sensors to 100% hydrogen decreases with the number of exposures and its recovery to baseline is increasingly less complete. In contrast, after an initial break-in period, the PdCr diode response to 100% hydrogen is nearly consistent with an equally consistent return to a common baseline.

The PdCr sensor is presently under development for use on the NASA experimental vehicle, the X-33, in its hydrogen leak detection system. A PdCr resistor, whose resistance is dependent on the hydrogen concentration, has been incorporated into the sensor design to expand the detection range of the sensor (Figure 1); a Schottky diode provides sensitive detection of low concentrations of hydrogen while the resistor provides sensitivity up to 100% hydrogen. Hardware and software ("Smart" electronics) have also been included with the sensor to provide signal conditioning and control.

This complete hydrogen detection system (two sensors on a chip with "Smart" electronics) has flown on the STS 95 mission of the Space Shuttle (launched 10-98) and again on STS 96 (launched 5-99). The hydrogen detection system was installed in the aft compartment of the Shuttle and used to monitor the hydrogen concentration in that region. Presently, a mass spectrometer monitors the hydrogen concentration in the aft compartment before launch, while after launch "grab" bottles are used. The inside of these "grab" bottles are at vacuum. During flight, the "grab" bottles are pyrotechnically opened for a brief period and the gas in the aft compartment is captured in the bottle. Several of these bottles are opened at different times during the takeoff and their contents used to determine the time profile of the gases in the aft chamber. However, this information is only available after the flight.

The data of the STS 95 mission has been analyzed. The response of the hydrogen sensors was compared to that of the mass spectrometer and those obtained by the "grab" bottles. During ground monitoring, the hydrogen sensor (Schottky diode) response paralleled that of the mass spectrometer but with a quicker response time. The hydrogen sensor response during launch and in-flight is shown in Figures 3. No sensor response is seen until the cut-off of the main engine. Near this time, a spike in the hydrogen concentration is observed which decreases with time back to baseline levels. These results are qualitatively consistent with the leakage of very small concentrations of unburnt fuel from the engines into the aft compartment after engine cut-off. These observations also agree with those derived from analyzing the contents of the grab bottles. Moreover, the advantage of this microsensor approach is that the monitoring of the aft compartment is continuous and, in principle, could be used for real-time health monitoring of the vehicle in flight.

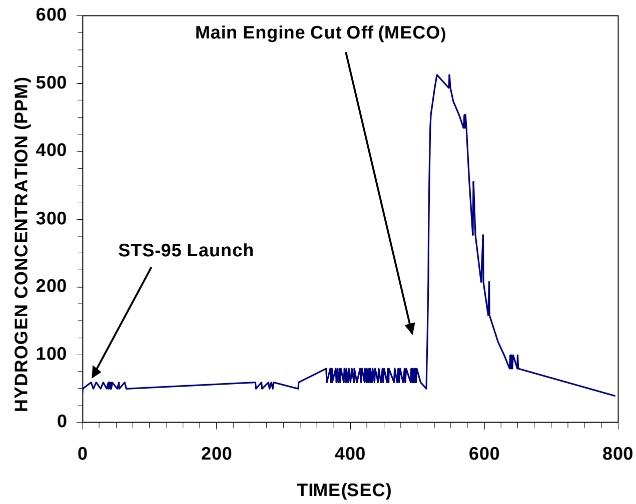


Figure 3. The response of PdCr Schottky diode sensor during the launch of the STS-95 Shuttle Mission.

<u>High Temperature Hydrogen and Hydrocarbon Detection</u>

The development of high temperature hydrogen and hydrocarbon sensors for use in harsh environments has centered on the development of a stable SiC-based Schottky diode. A Schottky diode is composed of a metal in contact with a semiconductor (MS) or a metal in contact with a very thin insulator or oxide on a semiconductor (MIS or MOS). For gas sensing applications, the metal is often a catalytic film. The advantage of a Schottky diode sensing structure in gas sensing applications is its high sensitivity. This is especially useful in emission measuring applications where the concentrations to be measured are low.

The detection mechanism for hydrogen, as discussed in the previous section, involves the dissociation of hydrogen on the surface of a catalytic metal. The atomic hydrogen migrates to the interface of the metal and the insulator, or the metal and the semiconductor, forming a dipole layer. This dipole layer affects the barrier height of the diode resulting in an exponential change in the current or a quadratic change in the capacitance. The magnitude of this effect can be correlated with the amount of hydrogen and other gas species (especially oxygen) present in the surrounding ambient atmosphere. The detection of gases such as hydrocarbons is made possible if the sensor is operated at a high enough temperature to dissociate the hydrocarbon and produce atomic hydrogen. The resulting atomic hydrogen affects the sensor output in the same way as molecular hydrogen (16, 21-23).

The Schottky diode structure under development at NASA GRC began with Pd on SiC MS structures (Pd/SiC). Direct contact between the catalytic metal and the semiconductor allows changes in the catalytic metal to have maximum effect on the semiconductor. Studies of this baseline system help determine limits of diode sensitivity, potential material interactions between Pd and SiC, and whether a barrier layer between the Pd and SiC is necessary for long-term sensor stability. The details of this work are reviewed elsewhere (22). The sensor detects hydrogen and hydrocarbons in inert or oxygen containing environments.

Figure 4 illustrates the advantage of SiC over Si in hydrocarbon sensing applications. Shown is the zero bias capacitive response of a Pd/SiC Schottky diode to one hydrocarbon, propylene, at a range of temperatures. The sensor temperature is increased from 100^{o}C to 400^{o}C in steps of 100^{o}C and the response of the sensor is observed. At a given temperature, the sensor is exposed to air for 20 minutes, N_2 for 20 minutes, 360 ppm of propylene in N_2 for 20 minutes, N_2 for 10 minutes, and then 10 minutes of air.

The magnitude of sensor response to 360 ppm propylene depends strongly on the operating temperature. A sensor operating temperature of 100^{o}C is too low for propylene to dissociate on the Pd surface, so the device does not respond at all. The three other curves for 200^{o}C, 300^{o}C, and 400^{o}C show that elevating the temperature increases the sensor's response to propylene. The presence of propylene can be detected at any of these higher temperatures with 200^{o}C being the minimum operating temperature determined in this study. Since the standard long-term operating temperature of Si is usually below 200^{o}C, these results demonstrate the significant advantages of using SiC rather than Si in gas sensing applications.

However, the sensor response is affected by extended high temperature heating. Prolonged heating at 425°C has been shown to change the sensor properties and to decrease sensor sensitivity (22). Even after heating at 425°C in air for 140 hours, the Pd/SiC Schottky diode is still very sensitive to the presence of hydrogen: a factor of 1000 change in forward current is observed upon exposure to 1000 ppm hydrogen in He. The reason for this change in diode properties is likely due to reactions between the Pd and SiC at the interface upon heating. Nonetheless, efforts have been underway to stabilize the sensor structure for long-term, high temperature operation. Two new structures have been demonstrated which improve the stability of the Pd-based Schottky diode structure over that of Pd/SiC (24).

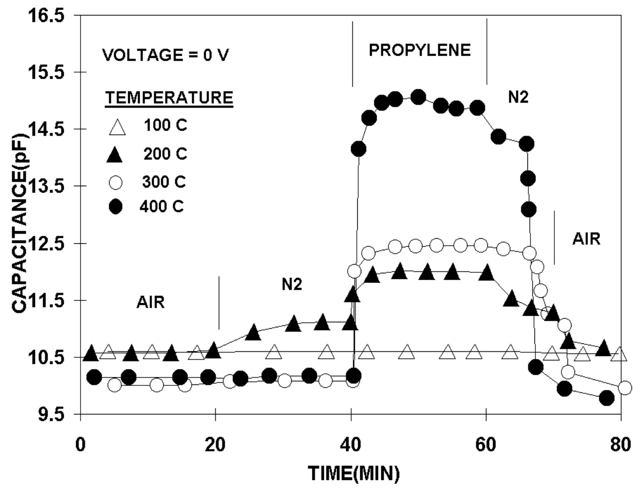


Figure 4. The temperature dependence of the zero bias capacitance to various gas mixtures. The response to propylene is seen to be strongly temperature dependent.

The first structure is PdCr directly deposited on SiC (PdCr/SiC). The advantages of PdCr as a high temperature alloy have been explored extensively in strain gage applications (25). It is a stable high temperature material which is able to provide static strain measurements at temperature up to 1100°C. However, its use in a gas-sensing SiC-based structure depends on not only its inherent stability but also such factors as the alloy's reactivity to SiC and the catalytic interactions of PdCr alloy with the gases to be measured.

Figure 5 demonstrates that PdCr/SiC is a viable diode structure for high temperature gas sensing applications with improved stability compared to Pd/SiC (22)). Shown is the response of a PdCr/SiC sensor as a function of heating time. The sensor is heated at 425°C in air for extended periods and then characterized at 100°C in air and upon exposure to a mixture of 120 ppm H_2 in N_2 (N_2/H_2 mix). While the air baseline current drifts lower with heating time, the current in the N_2/H_2 mix is relatively stable after the initial heating period of 40 hours. This results in the diode's sensitivity to H_2 (change from baseline) being nearly two orders of magnitude larger at this voltage after 250 hours of heating. Correspondingly, the magnitude of the signal in H_2 is nearly constant (within a factor of 3) after 40 hours.

The second structure involves the incorporation of chemically reactive oxides into the SiC-based Schottky diode structure. A wide variety of materials, e.g. metal oxides such as SnO_2, are sensitive to C_xH_y and NO_x at high temperatures. These materials could be incorporated as a sensitive component into MOS structures and, unlike silicon, SiC-based devices can be operated at high enough temperatures for these materials to be reactive to gases such as C_xH_y and NO_x. This results in a new type of gas sensitive structure: a metal-reactive oxide-semiconductor structure (MROS). The advantages of this type of SiC-based structure include 1) increased sensor sensitivity since the diode responds to gas reactions with not only the catalytic metal but with the reactive oxide as well, 2) improved sensor stability since the gas reactive oxide can act as a barrier layer between the metal and SiC potentially stabilizing the sensor's structure, and 3) the ability to vary sensor selectivity by varying the reactive oxide element.

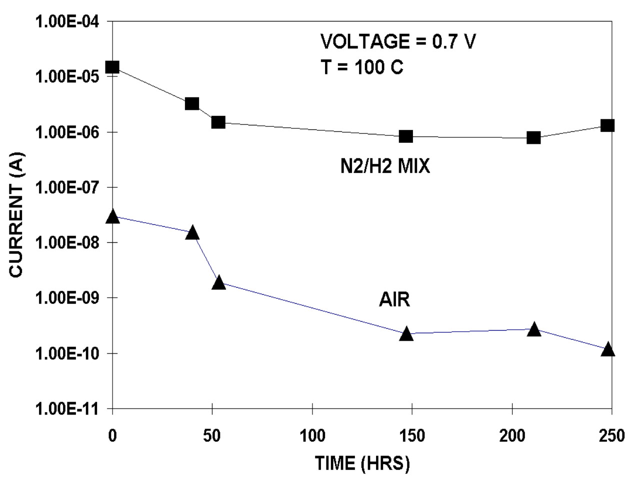


Figure 5. The forward current at 100°C vs heating time at 425°C in air (▲) and in 120 ppm H_2 in N_2 (■).

Figures 6-7 demonstrate the use of this type of MROS sensor by comparing the operation of a Pd/SnO_2/SiC sensor with a Pd/SiC sensor on the same chip. A thin (approximately 50 Å) SnO_2 layer covers the half the chip while the other half does not have SnO_2 present. Palladium contacts are sputter deposited on both sides of the chip. Two different carrier gases are used: pure N_2 and an air/N_2 mixture. The sensors are first exposed to air for 15 minutes, then the carrier gas for 15 minutes, followed by 400 ppm of a hydrogen-bearing gas in the carrier gas, 5 minutes of the carrier gas, and finally 10 minutes in air. The air/N_2 carrier gas had a constant oxygen concentration of 10%.

The effect of the thin SnO_2 layer is most easily seen in the I-V curves of Figure 6 for the Pd/SnO_2/SiC and Pd/SiC diodes respectively. The I-V curve for the Pd/SnO_2/SiC diode in Figure 6 shows parallel shunt resistance for voltages below 1.0 V, and exponential Schottky behavior above 1.0 V until series resistance effects begin to dominate. The barrier height derived from the exponential portion of the curves suggests that the SnO_2 increases the barrier height of the diode. The effect of the 400 ppm H_2 in N_2 on the I-V curve was to increase the current for a given voltage, with the increase in current in the shunt resistance region being somewhat lower than the increase in the Schottky region. This increase in current (resistance decrease) was also noted when the resistance across just the SnO_2 was monitored with probes under the same conditions. Thus, SnO_2 affects the response to hydrogen of the diode with higher sensitivity to hydrogen noted in the exponential Schottky-like conduction region. In contrast, the Pd/SiC diode shows two types of I-V behavior: an exponential response in the low voltage regions and a series resistance effects at higher voltages. These results clearly show that the SnO_2 changes the sensor's basic electronic behavior and the sensor response to H_2. Further research will investigate the effects of the geometry of the SnO_2 deposition on the sensor response as well as other the effect of other reactive materials beside SnO_2.

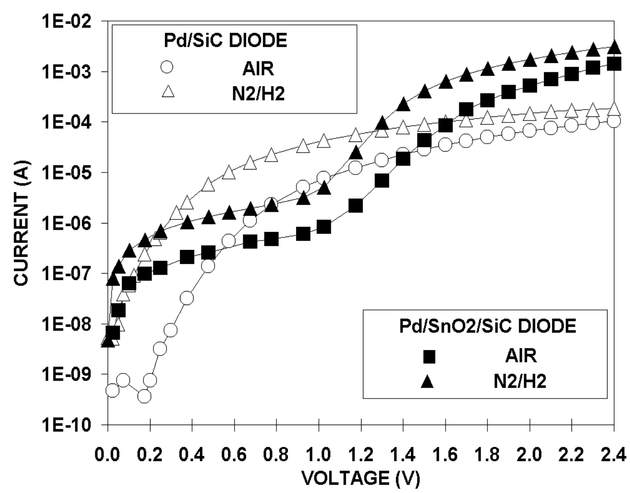


Figure 6. Current vs voltage at 350°C for a Pd/SiC diode in air (O) and the 400 ppm N_2/H_2 mix (Δ), and a Pd/SnO_2/SiC diode in air (■) and the N_2/H_2 mix (▲).

Figure 7 shows the response of both the Pd/SiC and the Pd/SnO_2/SiC diodes to H_2, methane, and propylene that were aged over a several week period at 350°C. The Pd/SiC sensor does not respond to 400 ppm of H_2 (Figure 7) or propylene and methane (not shown) in the air/N_2 mixture. However, the Pd/SnO_2/SiC sensor responds with increasing signal strength to methane, H_2, and propylene. That the Pd/SnO_2/SiC sensor response to propylene is stronger than that to H_2 is significant; the Pd/SiC response in N_2 (22) and in N_2/air to propylene and H_2 was reversed. Thus, the addition of the SnO_2 layer makes possible the detection of gases not detected without the layer. It should be noted that the response of the Pd/SiC sensor degraded over the several week period of 350°C operation while the Pd/SnO_2/SiC sensor remained relatively stable.

Other research includes the development of complete sensor packaging for the SiC-based sensor. The objective is to be able to package the sensor, with connections to external monitoring equipment, for operation in engine environments. Thus issues such as stable electrical contacts to SiC and the integrity of high temperature insulation are of importance.

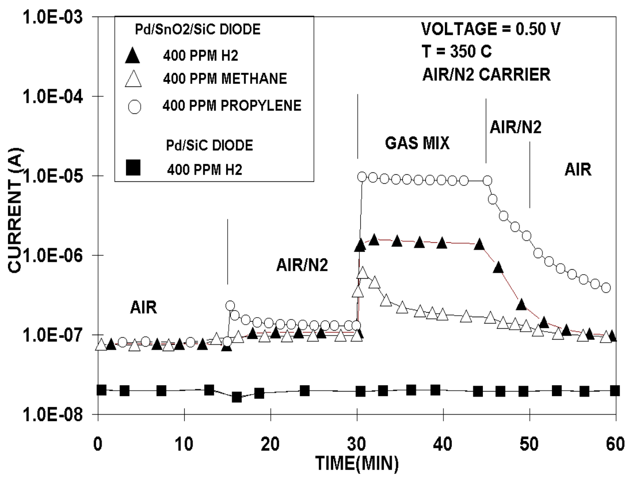


Figure 7. Current vs time at 350°C for a Pd/SiC diode exposed to 400 ppm H_2 (■) and a Pd/SnO_2/SiC diode exposed to 400 ppm of H_2 (▲), methane (Δ), and propylene (O).

Nitrogen Oxide (NOx) and Carbon Monoxide (CO) Detection

Two approaches are being explored for sensitive detection of NO_x (specifically NO and NO_2) and CO. First, the development of an MS or MIS SiC-based Schottky diode with a NO_x or CO sensitive structure as discussed in the previous section. Such a structure could use a catalytic gate (26) or a MROS structure. The general principles of operation of these types of sensors were discussed in previous sections.

The second approach to NO_x and CO detection is to use a microfabricated and micromachined Si-based structure. In contrast to the SiC-based approach where the SiC is used as a semiconductor, the Si in this approach is not an integrated part of the electrical sensing circuit. Rather, the Si is used as a platform on which the structure necessary for the sensor is fabricated. This sensor structure, shown in Figure 8, includes a temperature detector, heater, and sensing element. The microfabrication process allows the sensor to be small in size with low heat loss and minimal energy consumption. Energy consumption is further reduced by etching out the backside of the Si wafer so that the sensor components (temperature detector, heater, and sensing element) are over a diaphragm region. This minimizes the thermal mass of the sensing area thereby decreasing power consumption for heating and decreasing the time for thermal equilibrium. The temperature detector and heater are doped into the Si substrate for operation over a wide temperature range. The sensing element is composed of interdigitated electrode elements across which is deposited SnO_2. Changes in conductivity of doped SnO_2 across the interdigitated electrodes is measured and correlated to NO_x concentration.

A major component of this development work is to stabilize the SnO_2 for long-term, high temperature operation. Drift in the properties of SnO_2 with long term heating due to grain boundary annealing have been previously noted (27-28). This drift results in changes in the sensor output with time and reduces sensor sensitivity. In order to stabilize the SnO_2 structure for long term operation, the fabrication of nanocrystalline SnO_2, as shown in Figure 9, is being investigated. The grain size of the SnO_2 grains shown in Figure 9 are approximately 10 nanometers. Nanocrystalline materials have several inherent advantages over conventionally fabricated materials including increased stability and sensitivity at high temperature (29-30).

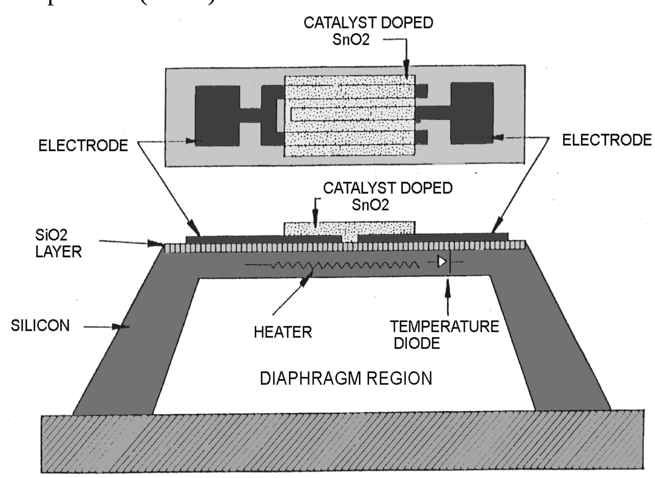


Figure 8. The structure of a tin-oxide NO_x sensor including temperature detector, heater, and sensing element. The electrode material is Pt and the sensor dimensions are approximately 300 microns on a side with a height of 250 microns.

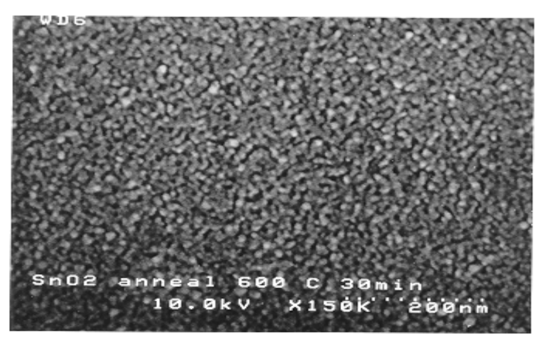


Figure 9. Nanocrystalline SnO_2 after annealing at 600°C for 30 minutes.

The parameters which affect sensor sensitivity to a given gas include device annealing temperature and doping of the grain boundaries. For example, annealing of the sensor at 700°C for 1 hour yields very high sensitivity (near a factor 10 change in resistance to 95 ppm CO at an operating temperature of 350°C) without significantly affecting the SnO_2 grain size. However, annealing of the sensor at 800°C for 1 hour significantly decreases the sensitivity (down to a factor of 3 for the same CO concentration under the same conditions) and generates a significant amount of SnO_2 grain growth.

Inclusion of materials in the grain boundaries can also significantly affect sensor sensitivity and stability. Figure 10 shows the response of a sensor doped with 5% Pt to a range of CO concentrations at 300°C in air. The sensor is very sensitive with a change in conductance of a factor of 38 from baseline to 95 ppm CO followed by a quick recovery. This is an increase of a factor of near 4 from the undoped sample. The detection of NO_2 at 360°C has also been achieved down to the 5 ppm level for a sensor annealed at 600°C. The sensor tends to saturate at higher NO_2 concentrations but the highest level of sensitivity is in the lower ppm range which is the region of interest. Work is beginning to increase the sensitivity, range, and selectivity of this NO_2 sensor through selective doping.

Further, the inclusion of silicia has been shown to significantly decrease the grain growth of the SnO_2 as shown in Figure 11: the inclusion of SiO_2 significantly inhibited particle growth of the grains after heating at 700°C for 24 hours. Work will continue to optimize processing conditions and doping concentrations of metals and silicates to improve sensor stability, sensitivity, and detection range for a given gas.

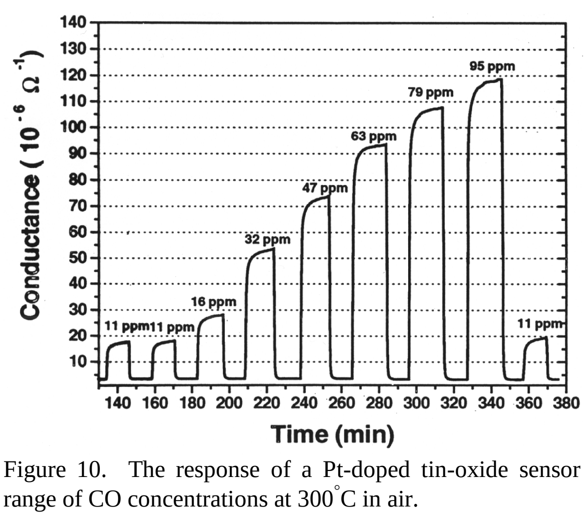
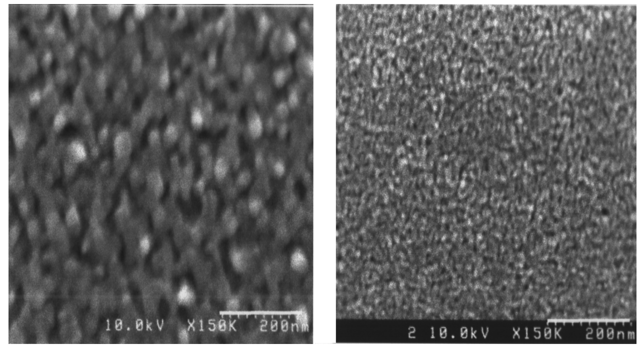


Figure 10. The response of a Pt-doped tin-oxide sensor to a range of CO concentrations at 300°C in air.



a) b)

Figure 11. Comparison of the effect of annealing at 700°C for 24 hours on an a) undoped SnO_2 film and b) 5 weight percent SiO_2 doped SnO_2 film. The SiO_2 doped film shows significantly improved stability (decreased grain growth) over the undoped film.

Oxygen Detection

The development of a microfabricated O_2 sensor has been initiated for safety purposes in aerospace applications but, as demonstrated in the automotive emissions control example, significant applications exist in the area of aeronautics emission control. Commercially available O_2 sensors are typically electrochemical cells using zirconium dioxide (ZrO_2) as a solid electrolyte and Pt as the anode and cathode. The anode is exposed to a reference gas (usually air) while the cathode is exposed to the gas to be detected. Zirconium dioxide becomes an ionic conductor of $O^{=}$ at temperatures of 600°C and above. This property of ZrO_2 to ionically conduct O_2 means that the electrochemical potential of the cell can be used to measure the ambient oxygen concentration at high temperatures. However, operation of these commercially available sensors in this potentiometric mode limits the range of oxygen detection. Further, the current manufacturing procedure of this sensor, using sintered ZrO_2, is relatively labor intensive and costly resulting in a complete sensor package with a power consumption on the order of several watts.

The objective of this research is to develop a zirconium dioxide solid electrolyte O_2 sensor using microfabrication and micromachining techniques. As noted in the previous two sections, the presence of O_2 often affects the response of hydrogen, hydrocarbon, and NO_x sensors. An accurate measurement of the O_2 concentration will help quantify the response of other sensors in environments where the O_2 concentration is varying. Thus, the combination of an O_2 sensor with other microfabricated gas sensors is envisioned to optimize the ability to monitor emissions.

A schematic of the sensor design is shown in Figure 12. As discussed in the NO_x detection section above, microfabricating the sensor components onto a micromachined diaphragm region allows the sensor to be small in size and have decreased energy consumption and time for thermal equilibrium. When operated in the amperometric mode, the current of this cell is a linear function of the ambient O_2 concentration. This linear response to oxygen concentration significantly increases the O_2 detection range of the sensor. A chamber structure with a well-defined orifice is micromachined to cover the sensing area. This orifice provides a pathway to control oxygen diffusion which is important in amperometric measurements. This orifice also protects the integrity of the sensing electrode from impinging particles. Preliminary testing of the complete O_2 sensor has been accomplished and further improvements on the design are planned.

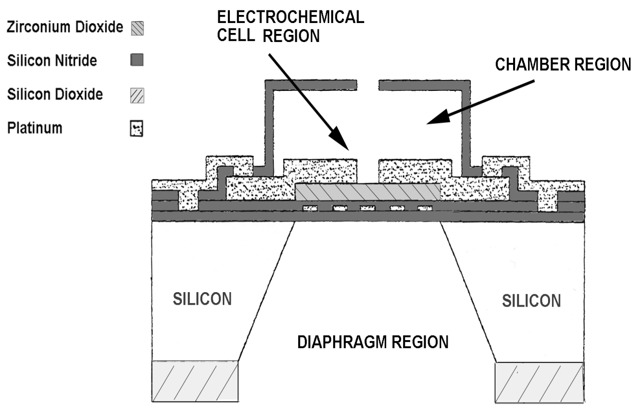


Figure 12. The structure of a microfabricated amperometric oxygen sensor. The dimensions of this sensor are comparable to that of the NO_x sensor shown in Figure 10.

<u>CO2 Detection</u>

The detection of CO_2 is, like the detection of oxygen, based on the use of a solid electrolyte. The significant difference between the O_2 sensor will be the use of NASICON (sodium super ionic conductor) as the solid electrolyte. NASICON is an ionic conductor composed of $Na_3Zr_2Si_2PO_{12}$ which has previously been shown to be sensitive for CO_2 detection. The preparation of the NASICON will be performed using a sol-gel technique. The sensor structure has similarities to that of Figure 8: a microfabricated, miniaturized sensor structure which can be incorporated with other sensors such as the CO sensor. The response of a NASICON-based sensor to a range of low CO_2 concentrations is shown in Figure 13. The sensor signal is the peak current derived from voltametric measurements. Effort is underway to further miniaturize the sensor and improve the response time. A combined CO_2/CO sensor is of interest not only for fire safety applications but for aeronautic combustion monitoring applications as well.

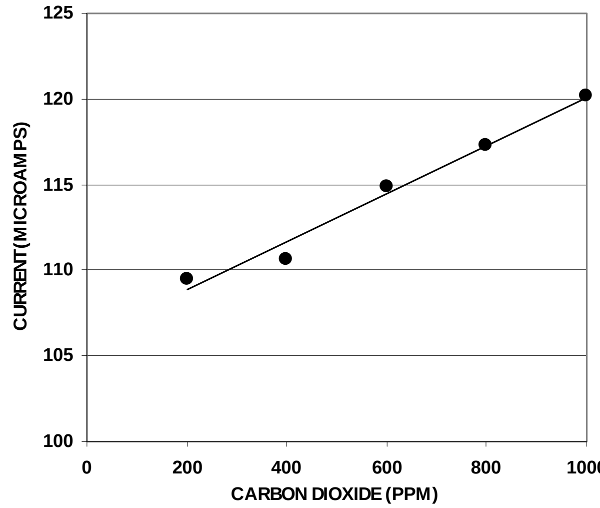


Figure 13. The peak current of a NASICON based sensor to range of CO_2 concentrations at 350°C.

<u>High-Selectivity Gas Sensors Based on Ceramic Membranes</u>

Gas sensors often rely on either the variation of a material property in response to a gaseous species, or the electrochemical transport of a species dependent upon its partial pressure. However, these sensors may have a lack of selectivity and display similar response to several different gaseous species. The selectivity of these sensors can be improved through the use of a selective membrane over the sensor to exclude other gaseous species which may interfere with the measurement of the species of interest.

A selective membrane with a narrow distribution of pore sizes may separate gaseous molecules according to molecular size, offering size selectivity to species of interest. Since the gas molecules of interest are on the order of several angstroms, the pore size would, likewise, need to be only several angstroms in diameter. Zeolites seem particularly well suited to this application. Zeolites are a crystalline ceramic material which contains open channels (or pores) as a natural part of its structure; they are also called microporous crystalline solids. Zeolites are composed primarily of aluminum, silicon, and oxygen. The elements combine to form SiO_4 and AlO_4 tetrahedra which are arranged to form three dimensional networks with uniform channels through the crystal. While these channels are identical in size or diameter within each structure of a zeolite, the diameters of theses channels can vary significantly (from 3 to 12 angstroms), depending mainly on the ratio of aluminum to silicon. Further, the effective diameters of the crystalline channels can be modified by the size of ions siting within the channels. Different ions may be incorporated into the crystalline channels by ion exchange. Still further, as a ceramic material, zeolites are capable of withstanding high temperatures and harsh environments which may be encountered during gas measurement.

Composite membranes containing zeolites are being prepared using various processing techniques to achieve desired selectivity, including sol-gel and electrochemical vapor deposition methods. The developed gas-selective membranes are also being integrated with various electrochemical sensors to further enhance the selectivity to gas molecules of interest.

High Temperature Electronic Nose Concept

The successful development of the individual high temperature sensors discussed above will allow the formation a sensor array which will allow the detection of a number of gases on a single chip. For example, the formation of an array of the sensors discussed in this paper will detect H_2, C_xH_y, NO_x, CO, CO_2 and O_2. These gases will be detected using three different platforms: a Schottky diode, a resistor, and an electrochemical cell. Further sensitivities can be achieved using the SiC-based MROS approach adding other materials (such as TiO_2, WO_3, $SrTiO_2$ etc.) into the SiC-based Schottky diode sensor structure. Each diode having a different reactive oxide will have a different sensitivity to the gases to which they are exposed. Improved selectivity and differentiation can be achieved using the ceramic membranes discussed above.

Development of a such a microfabricated gas sensor array operable at high temperatures and high flow rates would be a dramatic step in allowing the monitoring/control of emission produced by an aeronautic engine. This gas sensor array would, in effect, be a *high temperature* electronic nose and be able to detect a variety of gases of interest. Several of these arrays could be placed around the exit of the engine exhaust to monitor the emissions produced by the engine. The signals produced by this nose could be analyzed to determine the constituents of the emission stream and this information then used to control those emissions. The microfabrication of these sensors is necessary: a conventional bulky system would add weight to the aircraft and impede the flow gases leaving the engine exhaust.

The concept of an electronic nose has been in existence for a number of years. Commercial electronic noses presently exist and there are a number of efforts to develop other electronic noses. However, these electronic noses depend significantly on the use of polymers and other lower temperature materials to detect the gases of interest. These polymers are generally unstable above 400°C and thus would not be appropriate for use in harsh engine environments. Thus, a separate development is necessary for a high temperature electronic nose.

Work has begun on this high temperature electronic nose concept. As part of the Glennan Microsystem Initiative (31), CWRU, Ohio State University (32), and NASA GRC have begun to combine efforts in sensor technology, microfabrication technology, packaging, and software interpretation of sensor responses to develop a high temperature electronic nose which meets the needs of industrial applications.

COMMERCIAL APPLICATIONS

The gas sensors being developed by the Chemical Species Gas Sensors team at NASA GRC and its collaborators at CWRU, MEI, NASA KSC, and GIT are meant for aeronautics and aerospace applications but can be used in a variety of commercial applications as well. For example, the PdAg hydrogen sensors were developed for application on the launch pad of the space shuttle. These sensors were not completely developed for the space shuttle application due to the change in behavior at higher hydrogen concentrations. However, these sensors can be applied to an automotive application. GenCorp Aerojet Corporation, in conjunction with NASA Marshall Space Flight Center, has developed hardware and software to monitor and control the NASA GRC/CWRU sensors. The system can be customized to fit the user's needs, e.g., to monitor and display the condition of the tank of a natural gas vehicle. Several of these systems have been purchased for use on the Ford Motor Company assembly line for natural gas vehicles (NGV). This complete system received a 1995 R&D 100 Award as one of the 100 most significant inventions of that year.

MEI is continuing this work with potential application of hydrogen sensors in a variety of industrial environments. For example, use of a hydrogen sensor to detect degradation of the health of transformers is being explored. As electrical insulation in a transformer breaks down prior to its failure, hydrogen is released. Monitoring of hydrogen in-situ in these transformers can provide early detection of transformer degradation and avoid costly catastrophic failure of transformers in the field.

Likewise, the high temperature hydrogen, hydrocarbon, NO_x and oxygen sensors are being developed for aeronautics applications but can be applied in commercial applications. For example, the conditions in an aeronautic engine are similar to those of an automotive engine. Thus, sensors that work in aeronautic engine applications may be operable in automotive engine applications. NASA GRC has previously interacted with the Partnership for the Next Generation of Vehicles (PNGV) program regarding possible use of SiC-based technology for the sensing of hydrocarbons in automotive emissions. Other possible applications include combustion process monitoring, catalytic reactor monitoring, alarms for high-temperature pressure vessels and piping, chemical plant processing, polymer production, and volatile organics detection.

SUMMARY

The needs of space and aeronautic applications require the development of sensors with capabilities beyond those of commercial sensors. These requirements include operation in harsh environments, high sensitivity, and minimal size weight and power consumption. Sensor technology is being developed to address these requirements using microfabrication and micromachining technology as well as SiC semiconductor technology. High temperature gas selective membranes are also being developed to augment the capabilities of these sensors. The combination of these technologies allows for the fabrication of a wide variety of sensor designs with behavior and properties that can be tailored to the given application. Several types of sensors have been described all of which have aeronautic and space applications. Some of the sensor designs are relatively mature while the development of others is ongoing. The combination of these technologies may allow the development of a high temperature electronic nose to provide complex chemical analysis in harsh environments. Combination of these sensor technologies with hardware and software has already been accomplished in several applications.

Sensors designed for aeronautic and space applications also have significant commercial applications. One example is the use of the hydrogen sensor in automotive applications. This application involved a sensor not completely developed for a space application but with excellent properties for use in the automotive application. Further, given the similarities of aeronautic engine environments to those of automotive engine environments and chemical process monitoring, sensors developed for aeronautic applications also have a wide range of applicability. Although each application is different and the sensor needs to be tailored for that environment, the base technology being developed for aeronautic and space applications can have significant impact on a range of fields.

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31. For more information, see the web address: http\\www.glennan.org

32. Center for Industrial Sensors and Measurements, Ohio State University, http://cism.ohio-state.edu /mse/cism/home_page.html

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Aeronautic and space applications require the development of chemical sensors with capabilities beyond those of commercially available sensors. Areas of interest include launch vehicle safety monitoring, emission monitoring, and fire detection. This paper discusses the needs of aeronautic and space applications and the point-contact sensor technology being developed to address these needs. The development of these sensors is based on progress in two types of technology: 1) Micromachining and microfabrication technology to fabricate miniaturized sensors. 2) The development of high temperature semiconductors, especially silicon carbide. Sensor development for each application involves its own challenges in the fields of materials science and fabrication technology. The number of dual-use commercial applications of this microfabricated gas sensor technology make this area of sensor development a field of significant interest.

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